

LASER PYROLYSIS OF AN ENTRAINED STREAM OF COAL PARTICLES

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KEYWORDS: Coal Pyrolysis, Laser-heated, PCAH additives.

INTRODUCTION

In the search for efficient ways to convert coals to liquid fuels or other hydrocarbon products, the relative simplicity of pyrolysis has for a long time been recognized as a very attractive feature. However, char yields are typically high and volatile products are generally dominated by light hydrocarbons and tars that can be extremely difficult to upgrade. Efforts to guide research directed toward improved yields in pyrolysis processes have been hampered by the acceptance of a traditional mechanism that is, at best, incomplete (1).

In order to contribute to an improved understanding of the chemical and physical processes that control the formation of volatiles during coal pyrolysis, we have developed an apparatus for pyrolyzing coal particles entrained in cold gas with a CW infrared laser. (2) This approach results in very rapid in-depth heating of the coal to a steady-state temperature, which is determined by the balance between radiative input to the particle and the sum of convective and radiative heat losses to the cold gas. The advantages of this pyrolysis mode are that (i) it provides a very rapid heat-up to a steady state temperature and thus a close approximation to the idealized temperature-jump experiment; (ii) initially produced volatiles are evolved into a cold-gas atmosphere such that secondary reactions obscuring the nature of the original volatiles producing chemistry will tend to be minimized; and (iii) substantial quantities of coal are pyrolyzed making subsequent analysis of the tars and chars possible, something which is not possible with a single-particle approach. The difficulties of the approach involve the necessity to provide very constant flow rates and particle loadings and laser illumination that is constant with time and space in the heated region and is also reasonably omni-directional; the difficulties also involve the inescapable reality that even a narrow physical and aerodynamic particle size distribution will still result in some range of particle velocities, residence times, and steady-state temperatures.

A particular goal of this work is to use entrained-flow laser pyrolysis as one of the tools to explore the benefits that may be achieved by treating coals before pyrolysis with small amounts of high-boiling additives. The rationale for such an approach, along with some preliminary results using conventional heating methods, has been reported previously (3). In brief, in pyrolysis, meeting the stoichiometric and kinetic requirements of bond cleavage is especially crucial: not only is there no solvent to supply hydrogen as there is in liquefaction, but any hydrogen fed to the reaction zone is known (4) to be relatively ineffective at short reaction times and temperatures below $\sim 700^\circ\text{C}$. Therefore, it may be possible to achieve substantially increased yields of condensable volatiles, if pre-treatment with partially hydrogenated coal tars can (i) supply a small amount of critically needed hydrogen in a kinetically accessible form, and (ii) increase the efficiency with which the indigenous coal hydrogen can itself be shuttled from hydrogen-rich portions of the coal structure to more hydrogen-poor regions to aid in bond cleavage. Figure 1 summarizes the way by which polycyclic aromatic hydrocarbons (PCAH) tend to increase H-utilization efficiency in light of recently described chemistry (5-7): PCAH can serve to recover hydrogen atoms that have been transferred to positions where no linkage cleavage can occur. This recovery helps to re-direct hydroaromatic hydrogen from light hydrocarbon formation (ring-reduction and cracking) to cleavage of inter-cluster linkages.

LASER PYROLYSIS TECHNIQUE

Particle Flow

Schematic diagram of the laser-pyrolysis apparatus is shown in Figure 2. The coals are ground under nitrogen (or in the case of the Argonne -100 mesh samples, taken directly from the vials), wet-sieved, and dried for 18 hours under vacuum at 65°C. Several grams of the 270/230 mesh fraction (nominal 53 to 63 μm) are loaded into the hopper of a rotating-disc dust-feeder which feeds a fluidized bed, using argon as the entrainment gas. This bed in turn feeds the inlet of the 3-mm id ejector tube, the outlet of which is just downstream of an aluminum honeycomb flow straightener, and 3 to 5 mm upstream of the region where the IR laser beam crosses the axis of particle flow. The length of the illuminated region can be varied from 3 to about 20 mm. Condensable volatiles are either ejected from the pyrolyzing coal particles as an aerosol, or quickly form one when they hit the cold argon stream. Several mm downstream of the heated zone, the tar-aerosol and char particle stream enter a collector with an 8-mm id and a conical interior that smoothly decreases to 3 mm. The flow then passes through a miniature cyclone designed to collect particles larger than ca. 10 μm . The tar aerosol (typically 0.2 to 0.3 μm diameter), and any other small particles, pass through the cyclone and are collected on one of a pair of filters in a parallel-flow filter arrangement.

The char-tar separation is typically very good: microscopic examination shows the cake on the final filter to consist of tawny yellow tar aerosol particles, entirely free of black coal- or char-particles of any size. The cyclone contained all the char, with small amounts of tar aerosol attached to some of the char particles, evidently as the result of collisions within the cyclone. Since the aerosol particles were ca. 0.3 μm , as compared with the ca. 50- μm char particles, the mass fraction of tar contaminating the char was very low; typically less than 5%. This tar contamination could easily be removed from the char by a quick THF wash, either before char analysis, or for purposes of correcting the % yield of tar.

Gas Flow Control

The flow control system leading to and from the laser pyrolysis apparatus consists of four streams: the ejector- and collector- flows, and the ejector- and collector- sheath flows. Because flow through the ejector tube (ca. 50 cc/min) is not controllable directly, but is constrained to be equal to the sum of the collector- and the collector-sheath- flows minus the ejector sheath flow, and the two sheath flow are each about 5 liters/min, small percentage changes in either of the sheath flows would result in a large percentage change in the ejector flow. Therefore, fine positive control of the sheath gas is maintained by routing ca. 97% of their flow through single-stage regulators and over a fixed flow-control orifice. The remaining 3% is shunted through a pair of 0 to 500-cc/min mass flow controllers (Tylan). The flows are adjusted to control the ejector gas flow at the desired volumetric flow, typically set so that the ejector and its sheath flow have nearly equal space velocities.

Laser Beam Manipulation

The beam from a Coherent Model 41 CW CO_2 laser is passed through an 8-mm orifice in a graphite disc to remove the fringes, and is then directed to the cell by two flat and one slightly concave (20-m radius of curvature) copper mirrors. Immediately in front of the pyrolysis cell, the beam is focused through a point using a 1-in focal length zinc selenide lens, and allowed to expand into a channel integrator consisting of polished aluminum plates bolted together to form a channel having a 6.5-mm square opening. The divergent radiation that exits this channel is then imaged with a second lens through the KCl window in the pyrolysis cell and onto the axis of particle flow. The "beam" diverges after passing through the particle stream, and is re-imaged back on the flow axis by a concave copper mirror on the back side of the cell. The radiation that is not absorbed by the second pass diverges as it exits through the KCl window and is absorbed by a graphite beam block.

As shown schematically in Figure 3, the channel integrator converts the Gaussian profile of the laser beam into a profile that, on a microscopic scale, is flat across the entire image. Fresnel diffraction results in a series of peaks and valleys in the intensity, but these are on a microscopic

scale, with the peak-to-peak distance being ca. 200 μm , and are suitably averaged by retro-reflection under conditions where the stream of particles is optically thin.

Pretreatment of Coals and Product Analysis

The additive used in this work was a partially hydrogenated coal tar. The field ionization mass spectrum of the parent tar is shown in Figure 4. The spectrum clearly indicates that the tar is composed almost entirely of polycyclic aromatic hydrocarbons, with the most prominent PCAH structure being pyrene. In the spectrum obtained after hydrogenation (not shown), examination of the various M+2 and M+4 peaks shows that the degree of hydrogenation increases with increasing ring size. For example, ~22% of the pyrene, but 37% of the di-benzpyrenes were converted by the mild hydrogenation to di- or tetra- hydroaromatics. The coals were loaded with 8 to 10% of the hydrogenated tar, using tetrahydrofuran (THF) as the solvent employing the technique of incipient wetness to minimize preferential deposition of the additive at the particle surface and/or THF-extraction of soluble materials from the coal. The THF was removed by drying in a vacuum oven at 65°C for 18 hours. Some pyrolysis experiments were performed with THF-only treated coals to serve as appropriate blanks.

The primary analytical technique used thus far for examination of the tars and the chars has been field ionization mass spectrometry (FIMS). The use of the instrument at SRI has been extensively described in the literature (8); a series of unit-resolution mass spectra are recorded as the sample is heated in a temperature-programmed inlet (typically at 3°C/s, up to 450°C). From these data, the temperature evolution profile of any nominal mass or group of masses can be plotted, including a vacuum evaporation - or micro distillation- curve representing the sum of all volatiles. Although nominal mass provides no direct identification of the molecular formula of the particular molecular ion, in the low molecular weight range (m/z 50-150), and for prominent peaks at certain characteristic masses above that range, inspection can usually provide very reliable identification (8).

RESULTS AND DISCUSSION

The Impact of Pretreatment on Tar Yields

Figure 5 shows the impact of the tar pretreatment under laser-pyrolysis conditions, and for comparison, Figure 6 shows the impact observed under vacuum TGA conditions. (All of the yields were based on the assumption that the tar added in the pretreatment was itself fully volatilized.) Under the laser-pyrolysis conditions used thus far, the pretreated Pittsburgh No. 8 (Argonne) showed a substantial increase in tar yield (20%), but the pretreated Illinois No. 6 and Wyodak coals (Argonne), gave average corrected yields that were actually significantly lower than those for the untreated (but dried) coal. On the other hand, pyrolysis under TGA conditions resulted in 31 and 11% increases in yields of total volatiles for the pretreated Wyodak and Illinois No.6 coals, respectively, as well as an increase of 24% for the pretreated Pittsburgh No. 8 (Clovis Point Mine, and PSOC coals 1098 and 1099, respectively). The pretreated and the blank coals were not exactly identical in the two sets of pyrolysis experiments. However, for the reasons discussed below, we believe that the smaller benefit and less consistent improvement obtained under laser pyrolysis conditions resulted primarily from the fact that the final pyrolysis temperatures in the laser pyrolysis were more than 200°C higher. We therefore project that improving the yield-enhancing impact of the pretreatment entails pushing the laser-pyrolysis conditions further towards lower temperatures and longer times.

Since the amount of hydrogen actually supplied by the hydroaromatics added in the pretreatment is very small, it is important that this hydrogen be used with maximum efficiency, and that the added PCAH operate with maximum effectiveness in promoting the use of indigenous hydrogen. In order to meet these criteria, it is necessary to reach the temperature region of widespread radical reactions (i.e., 400 to 500°C), as these reactions are what bring about the H-atom transfer that results in hydrogenolysis. However, as the temperature increases, the PCAH in the reaction mixture are less and less able to recover hydrogen transferred to positions bearing no linkages (1,7). Optimum temperatures for conversion will thus be a compromise between reactivity and efficiency in hydrogen utilization.

We based our initial choice of conditions for the TGA pyrolyses that might constitute such a compromise on the work of Fong and Howard (9) on the evolution of volatiles and extractables

during coal pyrolysis. These authors report data showing that the yield of pyridine extractables generally goes through a maximum at the temperature at which the rate of volatiles production is highest. In general terms, this coincidence reflects the long recognized fact that in pyrolysis, an initially formed "bitumen" undergoes a disproportionation into a relatively hydrogen-rich volatiles fraction and a hydrogen-poor char fraction. As the temperature at which this disproportionation occurs is passed, the volatiles-forming reactions become progressively more dominated by gas-forming reactions such as dealkylation of small side chains, decarbonylation, and dehydrogenation, and production of large organic volatiles becomes no longer possible. Thus the maximum opportunity for influencing the "disproportionation" process so as to increase the volatiles and decrease the char will likely come at the point where the natural volatiles formation rate is the greatest, and before rapid H_2 formation squanders whatever hydroaromatic hydrogen is available in the additive or in the coal structure itself. We speculate that the best use of a hydrogen-donor additive in a pyrolysis process, where there is no large confining pressure, will be made by going very rapidly to this temperature region, and then holding the temperature there.

In the rapid heating (1000°C/s) studies of Fong (9), the maximum volatiles formation rate occurred at a nominal temperature of about 600°C , but at the maximum heating rate achievable in the TGA apparatus used in this work ($< 7^\circ\text{C/s}$), the volatiles formation rate was maximum at about 450°C . Therefore, we tested the impact of additives by raising a furnace, previously heated to 900°C , around the quartz tube containing the sample, and when a temperature of 450°C was reached, quickly lowering the furnace. Since the quartz tube cooled slowly compared to the rate at which it was heated, this procedure approximated the desired regimen, but the heating rate was slow enough that blank experiments with the tar additive loaded onto charcoal showed that a large fraction of the tar additive vaporized by the time the pretreated coal reached 450°C .

By comparison, the laser-pyrolysis, with a heating rate of about $10,000^\circ\text{C/s}$, should bring the pretreated coal to ca. 500°C while most of the additive is still within the coal matrix. Since the temperature of maximum volatiles formation in a linear heating-rate experiment is a function of heating rate, we expect the optimum temperature with laser-heating to be 100 to 200°C above that for the slower heating-rate pyrolysis. Unfortunately, the data shown in Figure 5 were generated when the residence time or "hold time" at maximum temperature was only ~ 0.1 s, and substantial tar formation is not observed in this short a reaction time unless the final temperature is above 700°C . We chose an upward flow in the pyrolysis cell to move the particles as slowly as practical. However, the distributions of aerodynamic particles sizes used thus far have not been narrow enough to allow successful entrainment at space velocities less than ca. 10 cm/s above the nominal settling velocity of $50\text{-}\mu\text{m}$ coal particles. We anticipate that the use of coal particles having a narrower aerodynamic size distribution, as well as a narrow physical size distribution, will enable us to improve the entrainment and increase the residence time to 0.5 to 1 second, and thus to lower the final pyrolysis temperature substantially.

Characteristics of Laser-Pyrolysis Tars

The tars produced by pyrolysis of the coals in a stream of cold gas, and as collected on the final filter, consist of agglomerates of light yellow spheres, quite evenly sized at about 0.2 to 0.3 μm . Although they contain substantial amounts of rather low boiling materials (e.g., phenol, cresols), these aerosol particles are not very sticky at room temperature, and do not coalesce when scraped of the filter with a spatula. Upon exposure to air at room temperature, they turn black in several hours.

Several samples of the laser pyrolysis tars have been subjected to FI mass spectrometry. Figure 7 shows the spectra obtained for the tars from the Argonne Pittsburgh No. 8 and Wyodak coals. The volatility of the tars, under the FIMS analysis conditions (heated to 450°C at 3°C/s under a vacuum $\leq 10^{-6}$ Torr) ranges from 57% for some of the Illinois No. 6 tars, to 90% or above for the Pittsburgh No. 8 and Wyodak tars. Since any fossil fuel material that has been through a distillation process (whether atmospheric or vacuum) is typically completely volatile ($> 95\%$) in FIMS analysis, either a substantial part of the Ill. No. 6 tar is ejected as an aerosol without ever being in the vapor phase, or retrograde reactions converted a substantial fraction into non-volatile materials. Since the tars are ejected into a cold, inert atmosphere, where the cooling rate is in excess of 1000°C/s , we judge that any retrograde reactions that did not occur before the tar left the hot coal particle would be unlikely to occur after leaving. Thus the FI mass spectral analyses that are discussed below should be considered representative of the tar as it left the coal particle.

The yields of tars produced in the laser pyrolysis appear, as shown in Table 1, to be about 1.5 times larger than those obtained by Khan et al. (10) in a hot-gas, entrained-flow reactor (hot-tube EFR reactor) with a final temperature of 1100°C. However, uncertainty over what fraction of materials detected in the vapor state (e.g., "olefins") in the work of Khan would be found in the tar from the laser pyrolysis precludes a definitive comparison at this time. Therefore in this report we will focus on some of the differences in the character of the tars produced from the Argonne Pittsburgh No. 8 and Wyodak coals using each of these two rapid-heating entrained-flow pyrolysis techniques. (We reiterate that laser-pyrolysis has no process implications as such. The use of an IR laser in laboratory studies has value insofar as it leads to an increase in fundamental understanding and/or in the ability to improve yields in technologically important processes.)

In general terms, the tars from the Pittsburgh coal are rather similar, whereas those from the Wyodak show some marked differences. For example, in the Pittsburgh tars, the fractions constituted by cresols, dihydroxybenzenes, and the sum of alkylbenzenes and tricyclic alkanes are equal within 30%. However, in the Wyodak tars, the percents of dihydroxybenzenes and the most abundant acyclic alkanes are three and two times larger, respectively, in the laser-pyrolysis tar than in the hot-tube tar. Thus, in the tar that was evolved into a cold gas stream, the abundance of what is presumably the most retrogression-prone class of phenolics -- dihydroxybenzenes -- is substantially higher. What is perhaps more surprising is that the concentration of certain alkanes is also higher in the laser pyrolysis tars. Although there is hardly enough evidence yet to draw a definitive conclusion, a possible rationalization is that when the dihydroxybenzenes (or their precursors) undergo retrograde reactions, they tend to take the some of the alkanes (or their precursors) with them.

A still more striking comparison is that between the FI mass spectra of the laser-pyrolysis tar and that produced from the in-situ pyrolysis of the Wyodak coal in the temperature-programmed inlet of the mass spectrometer (Py-FIMS); the latter is shown in Figure 8. In the spectrum of the laser-pyrolysis tar (Figure 7b) the highest peak among the phenolics (m/z 124, methylidihydroxybenzene) and the highest peak of the acyclic alkanes show intensities that are within 40% of each other, whereas in the Py-FIMS, the intensity of m/z 124 is three times that of m/z 268. Because any volatiles produced during Py-FIMS are evolved into a high vacuum, there is negligible opportunity for secondary gas phase reactions; therefore, any increased retrograde reaction under Py-FIMS conditions must be a result of a heating rate that is about three thousand times slower. At this point we cannot say whether the relative enhancement of such retrograde processes is an inherent result of reaction at lower temperatures during the slow heating, or merely reflects a greater chance for retrograde reaction during the slower transport of volatiles once they are generated within the coal.

Comparison of the temperature evolution curves for the most abundant single-ring monohydric and dihydric phenols (xlenols and methyl dihydroxybenzenes) reveals a rather striking difference between the tars from the two entrained flow techniques. Figures 9 and 10 show that in the laser-pyrolysis tar essentially all of the material in both classes is preexisting in the tar. In the tar generated in the hot-tube reactor on the other hand, most of the monohydric phenols and a good part of the dihydric phenols are pyrolytically generated on the hot probe during the FIMS analysis, as seen from the fact that they are observed at much higher temperature. The difference between the two types of tars is even more pronounced than it appears in Figures 9 and 10, since what is plotted there is the fraction of the total observed in each case for each molecular ion. As shown in Table 1 and discussed above, for the Wyodak coal, the total amount of dihydric phenols in the laser pyrolysis tar is 3.3X higher than that seen in the EFR tar.

The above differences cannot be attributed entirely to a different distribution of volatiles between gases and tars in the two pyrolysis techniques. Since the hot-tube reactor tars were produced by heating the coal to 1100°C and the tars were originally evolved into a hot nitrogen stream, one might have expected the relatively low-boiling phenols to have been much more "distilled" out of the tars during the collection, and a greater fraction of those low molecular phenols that were seen might be expected to have been formed by pyrolysis on the hot FIMS probe. However, in three of the four curves shown, the situation with the laser pyrolysis tars was not merely that there were more preexisting phenols, but that there was essentially no phenol generation during analysis of the laser-pyrolysis tars. Thus we are forced to say that even though one might have expected the higher temperature, longer residence time, and hot-gas atmosphere in the EFR to have produced tars that were more "evolved" and therefore more refractory, they were

not more refractory. It could be that the greater opportunity for oxidative coupling reactions provided by the hot-gas environment of the hot-tube reactor provides coupling products of dihydroxyaromatics that subsequently gave monophenols on the heated FIMS probe. This scenario would be consistent with the substantially lower levels of dihydroxybenzenes seen in the Wyodak hot-tube tars, and also with the higher total tar yields observed in the laser pyrolysis.

In summary, although the chemistry responsible for formation and evolution of oxygenates in coal tars is still largely unknown, the above data from laser pyrolysis in a cold-gas atmosphere are helping to delineate the factors that control the types and amounts of phenolic structures present in pyrolysis products. At this stage, we can make the following tentative conclusions:

- The laser-pyrolysis tar yields appear to be higher than from those produced in hot-tube pyrolysis of the same coals at equal or greater severity.
- The differences between entrained-flow laser-pyrolysis tars and entrained-flow hot-tube pyrolysis tars are much greater for Wyodak coal than for Pittsburgh No. 8 coal.
- The laser-pyrolysis tars contain substantially more low-molecular weight monophenolic and diphenolic structures than do the entrained-flow hot-tube pyrolysis tars.
- These phenolics, which undergo facile oxidation, are presumably responsible for the initial pale yellow tars turning black upon exposure to air.

REFERENCES

1. D. F. McMillen, R. Malhotra, S. E. Nigenda, *Fuel*, **1989**, *68*, 380.
2. D. F. McMillen, R. Malhotra, M. W. Smith, "Cleavage and Crosslinking of Polymeric Coal Structures during Pyrolysis," DOE Quarterly Report, Contract No. DE-AC21-87MC23286, August 1989.
3. R. Malhotra, G. A. St. John, D. S. Tse, D. F. McMillen, *Am Chem Soc, Div Fuel Chem. Preprints*, **1988**, *33*(2), 257.
4. J. B. Howard, "Fundamentals of Coal Pyrolysis and Hydropyrolysis," in *Chemistry of Coal Utilization*, Second Supplementary Volume, M. A. Elliott, Ed., John Wiley and Sons, New York, 1982, p. 665.
5. D. F. McMillen, R. Malhotra, S.-J. Chang, W. C. Ogier, S. E. Nigenda, R. H. Fleming, *Fuel*, **1987**, *66*, 1611.
6. R. Malhotra and D. F. McMillen, "A Mechanistic Numerical Model for Coal Liquefaction Involving Hydrogenolysis of Strong Bonds. Rationalization of Interactive Effects of Solvent Aromaticity and Hydrogen Pressure," , submitted to *Energy and Fuels*.
7. D. F. McMillen, R. Malhotra, and D. S. Tse, "Interactive Effects Between Solvent Components: Possible Chemical Origin of Synergy in Liquefaction and Coprocessing," , submitted to *Energy and Fuels*.
8. See, for example: M. M. Boduszynski, *Energy and Fuels*, **1987**, *1*, 1
9. W. S. Fong, W. A. Peters, and J. B. Howard, *Fuel*, **1986**, *65*, 251.
10. M.R. Khan, M. A. Serio, R. Malhotra, and P.R. Solomon, *Am. Chem. Soc, Div. Fuel Chem. Preprints*, **1989**, *34*(4), 1054.

YIELDS OF TAR AND SELECTED PHENOLIC AND ALIPHATIC COMPOUNDS IN LASER- AND HOT-TUBE¹-COAL PYROLYSIS

Coal	Pyrolysis Technique/ Run No.	T _{final} °C	% Tar Yield ²	Tar/ Char	% FIMS ³ Volatility	% Total Ion Intensity ⁴			
						m/z			
						122	124	260	268
WYODAK (Argonne)	LP/6-8-89-3	750	17.4	0.28	90	0.18	0.77	0.43	0.63
Pitts No. 8 (Argonne)	LP/6-13-89-2	925	27.4	0.64	92	0.11	0.11	0.38	0.24
ILL No. 6 (Argonne)	LP/5-26-89-1	880	29.2	0.57	71	0.13	0.29	0.36	0.34
WYODAK (Argonne)	HT	1100	7.71	0.18	86	0.067	0.23	0.31	0.32
Pitts No. 8 (Argonne)	HT	1100	21.84	0.46	63	0.075	0.057	0.18	0.30

¹Data taken from the hot-tube entrained-flow pyrolysis results in Reference 10.

²In LP, % tar yield is derived from the collected weights of tar and char, by assuming the same gas yield reported in the 1100°C, hot-tube pyrolyses of reference 10. This gas yield will be an over-estimate, because of both the lower final coal temperatures of the LP runs and the cold gas atmosphere in the laser pyrolysis.

³Wt. % volatilized from probe at 450°C under high vacuum.

m/z 122 corresponds to methylcresols, 124 to methyl-dihydroxybenzenes, 260 nominally to tetra-cyclic alkanes and alkyl-benzenes, and 268 nominally to acyclic alkanes. The % ion intensity values do not exactly equal mole %, owing to differences in sensitivity factors. However, the relative % changes in intensity values from one sample to another are expected to be reliable.

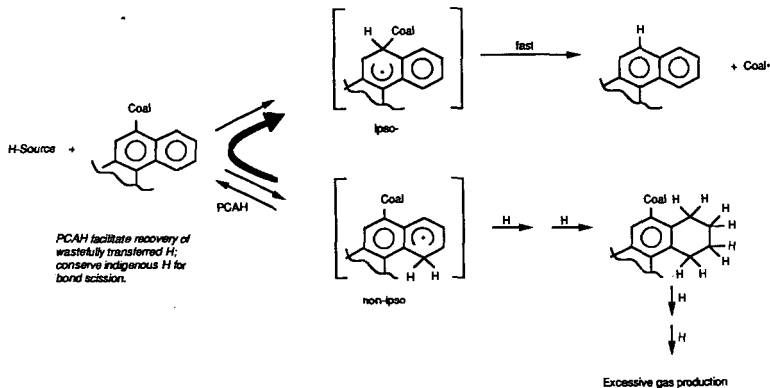
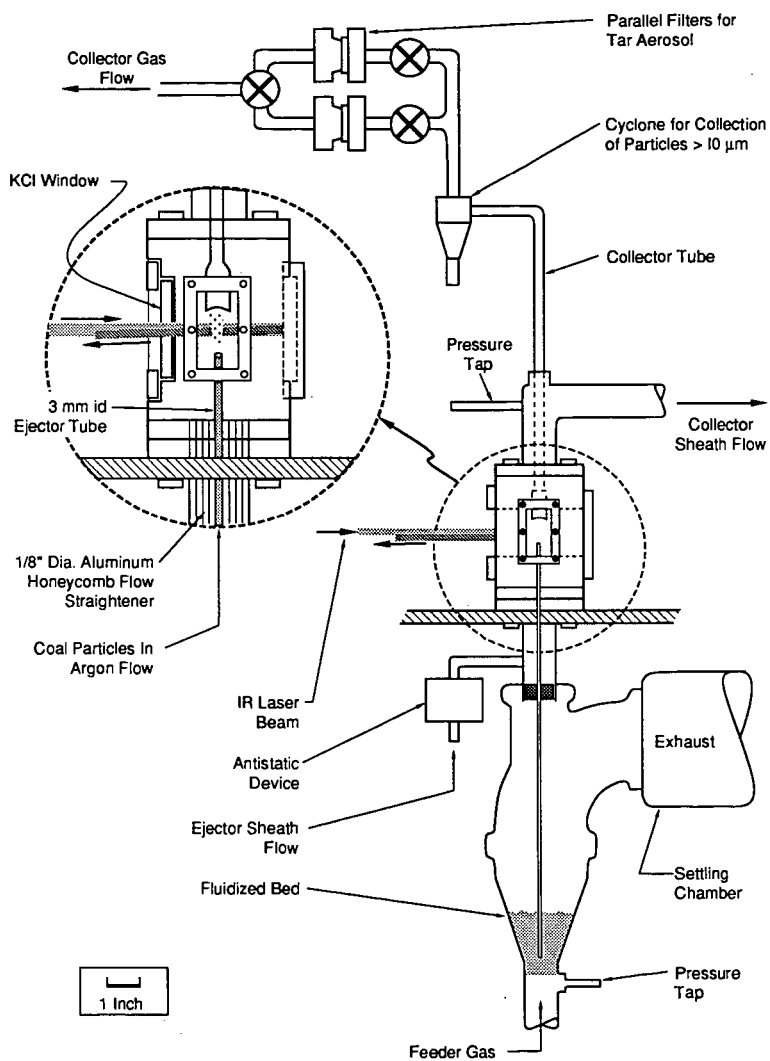


Figure 1. Rationale for Using Additives Rich in Polycyclic Aromatic Hydrocarbons (PCHAH).

Premises: 1. Significant contribution of induced bond cleavage.

1. Significant contribution of induced bond cleavage.
2. Factors enhancing IBS also tend to minimize retrogressive reactions.



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Figure 2. Schematic of entrained-flow laser pyrolysis apparatus.

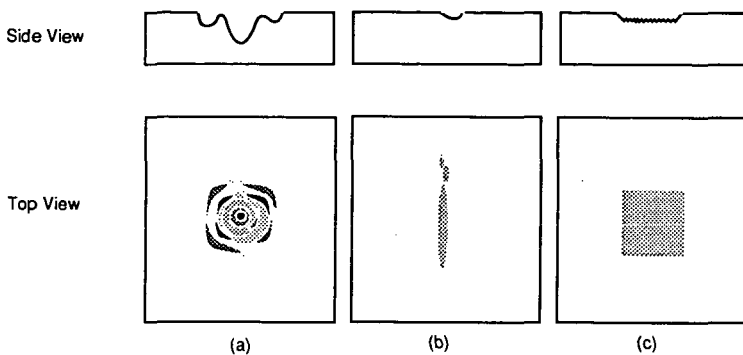


Figure 3. Schematics of burn patterns produced in acrylic pieces using (a) apertures, (b) beam expander, or (c) channel integrator in the optical configuration.

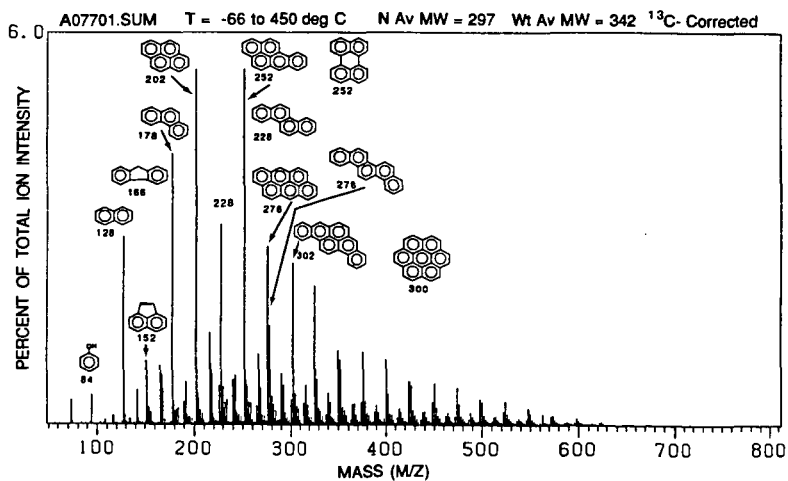


Figure 4. Field ionization mass spectrum of the coal tar prior to hydrogenation.
Note that the tar is rich in PAH essentially devoid of alkyl substitution.

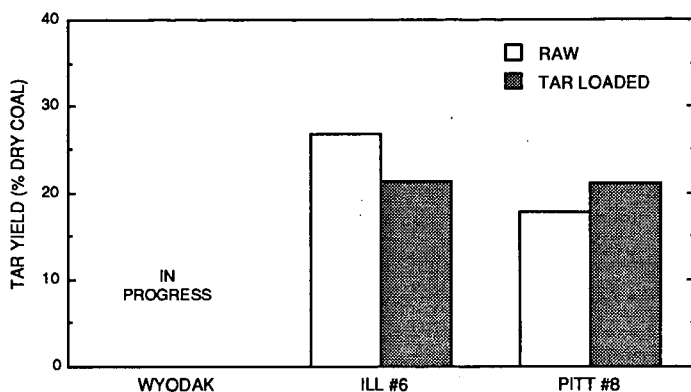


Figure 5. Effect of loading hydrogenated coal tar on the tar yield during laser pyrolysis. Maximum temperature of about 880°C for the ILL #6 coal and 840°C for Pitt. #8 coal.

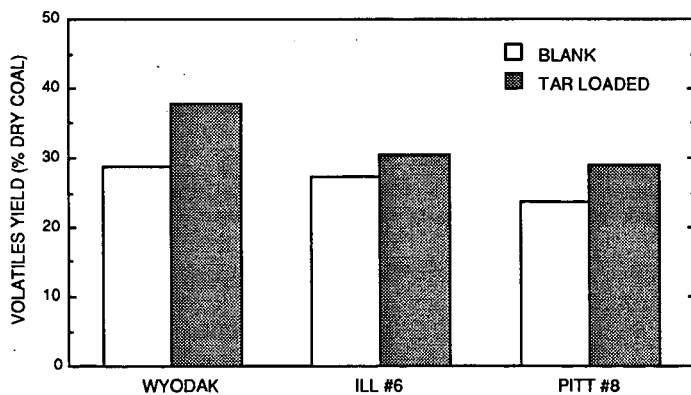
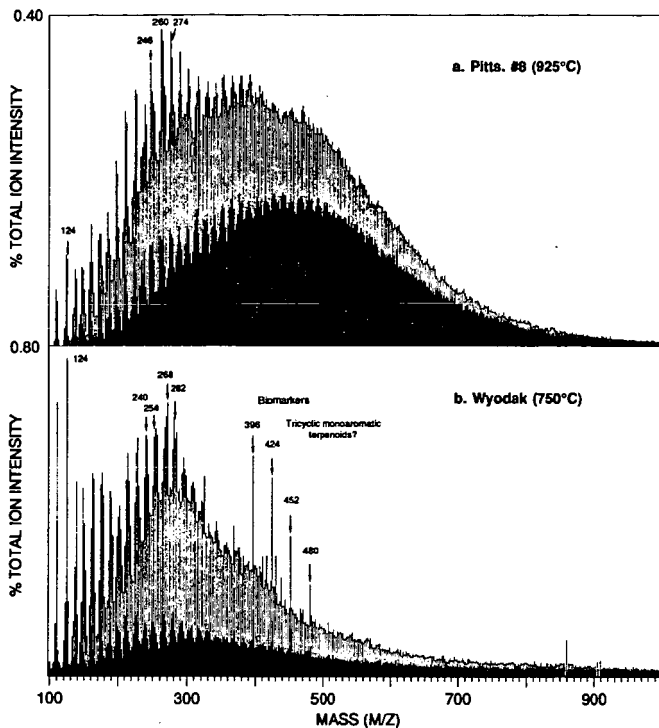


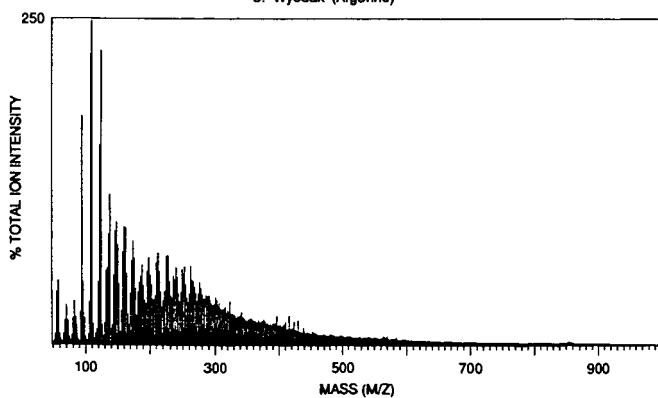
Figure 6. Effect of loading hydrogenated coal tar on volatiles yield during vacuum pyrolysis to a maximum temperature of about 450°C.



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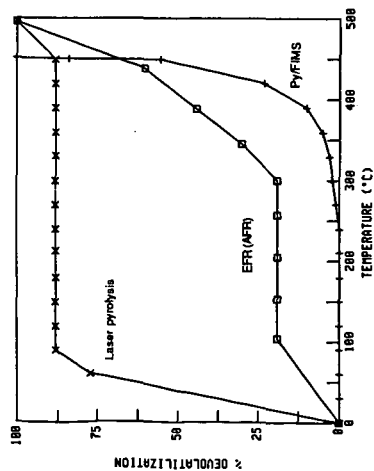
Figure 7. FI mass spectra of laser pyrolysis tars.

- a. Pittsburgh No. 8 (Argonne)
- b. Wyodak (Argonne)



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Figure 8. Py-FIMS of Wyodak coal (Argonne Premium Coal Sample Program).



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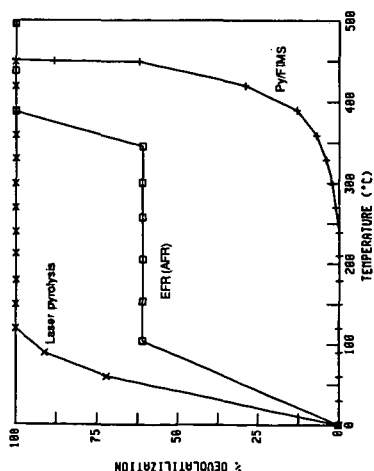


Figure 9. Temperature evolution profile of phenolics during FIMS analysis of laser-pyrolysis tar and tar from entrained flow pyrolysis in a hot tube (EFR), compared with the evolution during in-situ pyrolysis in the FI-mass spectrometer (Py-FIMS) of the Argonne Pittsburgh No. 8 coal.
(a) monohydric phenols (m/z 122); (b) dihydric phenols (m/z 124)

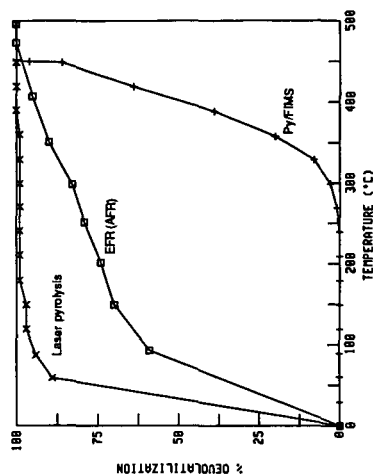
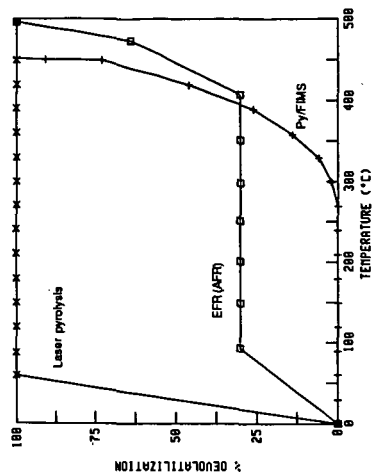


Figure 10. Temperature evolution profile of phenolics during FIMS analysis of laser-pyrolysis tar and tar from entrained flow pyrolysis in a hot tube (EFR), compared with the evolution during in-situ pyrolysis in the FI-mass spectrometer (Py-FIMS) of the Argonne Wyodak coal.
(a) monohydric phenols (m/z 122); (b) dihydric phenols (m/z 124)